

Borazine

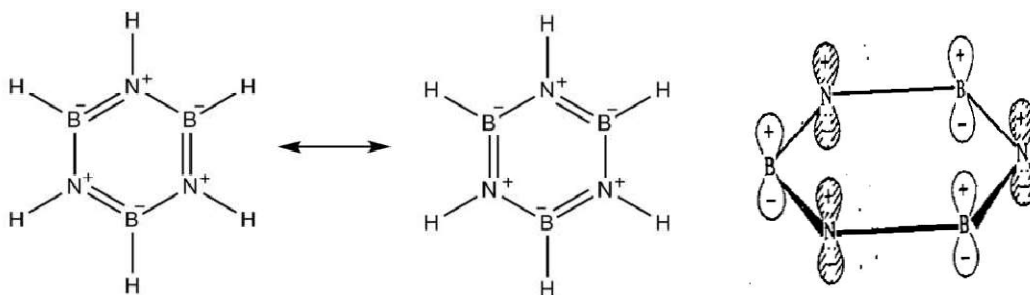
Borazine or Borazole ($B_3N_3H_6$): Borazines are colourless liquid and isoelectronic with benzene and hence they are also called **inorganic benzene**.

Structure: Various chemical reactions and electron diffraction studies shows that borazine is isoelectronic with benzene and hence its structure is the same as that of benzene. Like benzene, borazine has a planar hexagonal structure, containing 6 membered ring, in which B and N atoms are arranged alternately. Because of the similarity between the structures of borazine and benzene, borazine is called inorganic benzene.



In Borazine both boron and nitrogen are sp^2 hybridised. Each N-atom has one lone pair of electrons, while each B-atom has an empty p-orbital. (B-N) -bond in borazine is a dative bond, which arises from the sidewise overlap between the filled p-orbitals of N-atom and empty p-orbitals of B-atom.

Since borazine is isoelectronic with benzene, both the compounds have aromatic electron cloud. Due to greater difference in electronegativity values of B and N-atoms, the electron cloud in B_3N_3 ring of borazine molecule is partially delocalised (since N orbitals are of lower energy than the B orbitals). While in case of benzene ring, the electron cloud is completely delocalised.



M.O calculations have indicated that electron drift from N to B is less than the electron drift from B to N, due to greater electronegativity of N-atom. For this N atoms become relatively more negative than B atoms. In benzene molecule, C=C bonds are non polar, while in case of $B_3N_3H_6$,

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due to the difference in electronegativities between B and N atom, B-N bond is polar. It is due to the partial delocalisation of electron cloud that bonding in B₃N₃ ring is weakend.

N-atom retains some of its basicity and B atom retains some of its acidity. Polar species like HCl, therefore, attack the double bond between N and B. i.e why borazine in contrast to benzene, readily undergoes addition reaction. The electrophile H⁺ attacks to the partially negative end N-atoms and the negative groups add to the partially positive end B-atoms through nucleophilic attack. In borazine B-N bond length is equal to 1.44Å, which is between calculated single B-N bond (1.54 Å) and B=N double bond length (1.36 Å). The angles are equal to 120°. In benzene C-C bond length is 1.42 Å.

Preparation of borazine:

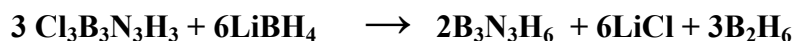
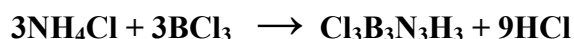
1. Stock and Pohlands method: By the action of NH₃ on Diborane (B₂H₆). The adduct B₂H₆.2NH₃ is first formed which then gets decomposed by heating in a closed tube at 200 degree Celsius.



(Ratio=1:2) Adduct

This method gives low yield because of simultaneous formation of solid polymeric by-products.

2. Heating BCl₃ with NH₄Cl: Heating BCl₃ with NH₄Cl in chlorobenzene (C₆H₅Cl) in the presence of Fe, Ni, or Co(as catalyst) at about 140 degree celsius B₃N₃H₆ is formed. This derivative being reduced with LiBH₄ in polyether, gives borazine.



3. By heating a mixture of LiBH₄ and NH₄Cl: B₃N₃H₆ can be prepared in the laboratory by heating a mixture of LiBH₄ and NH₄Cl in vacuum at 230 degree celsius.



This method gives 30% Borazine.

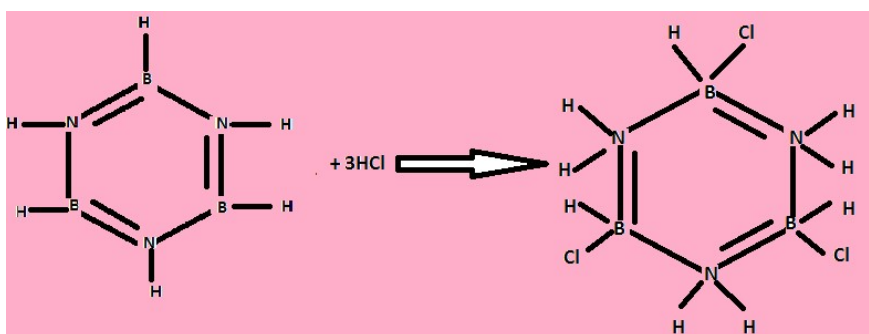
Physical properties: Borazines are colourless volatile liquid. Molecular weight : 78 g

Boiling point : 64.5°C, Melting point : -58°C, Decomposes at -80° C

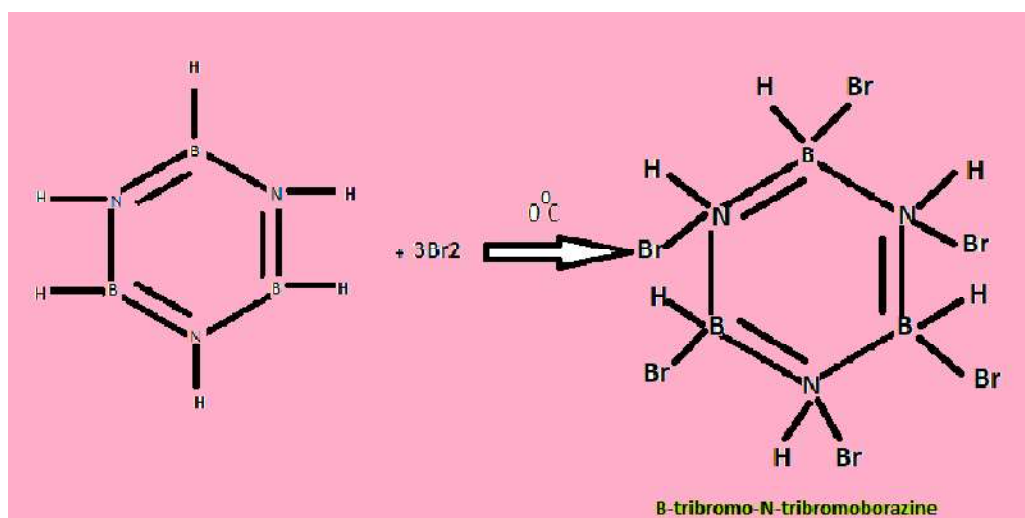
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Chemical properties:

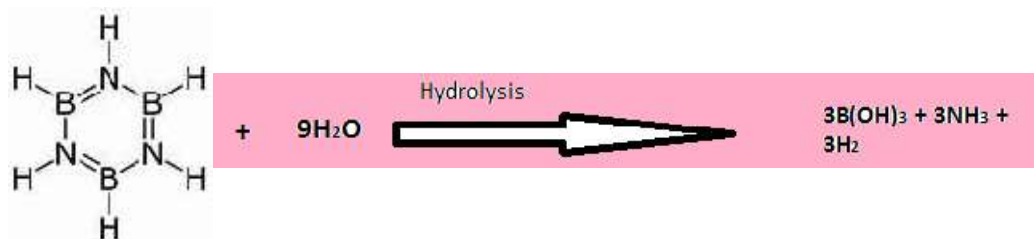
1. **Addition reactions:** One molecule of borazine adds 3 molecules of HCl or HBr in the cold without a catalyst. These molecules get attached with all the three B atoms of borazine, since B atom is more negative than N atom in B-N or B=N bond and hydrogen chloride derivative is obtained. This addition reaction is not shown by benzene.



One molecule of borazine adds to 3 molecules of Br₂ at 0 °C and gives B-tribromo-N-tribromoborazine.

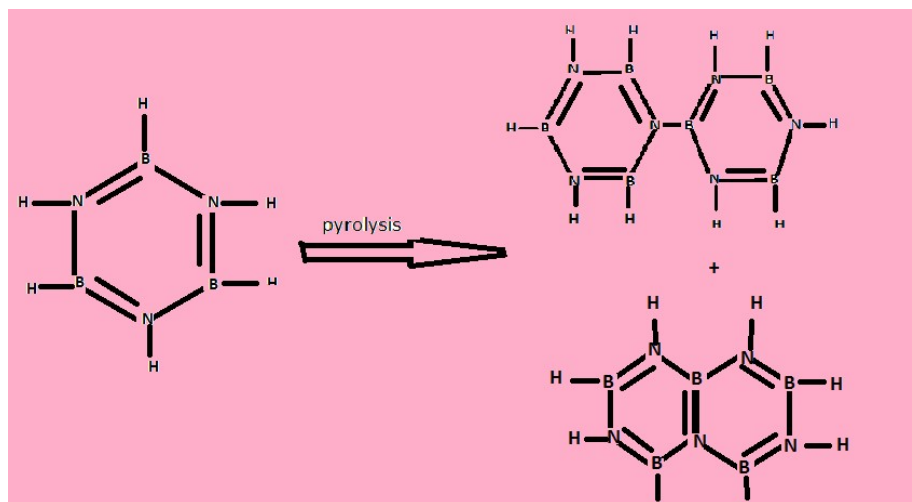


2. **Hydrolysis:** Borazine gets slowly hydrolysed by water to produce boric acid, ammonia and Hydrogen. Hydrolysis is favoured by the increase in temperature.

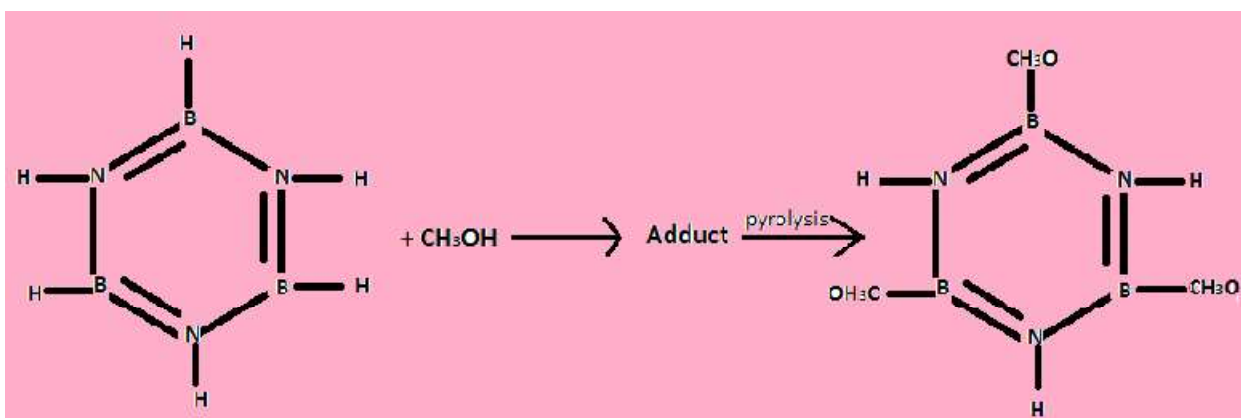


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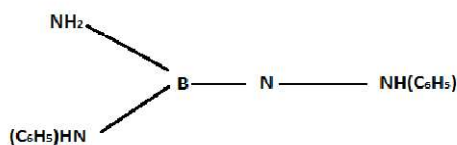
3. Pyrolysis: When borazine is pyrolysed above 340°C , $\text{B}_6\text{N}_6\text{H}_{10}$ and $\text{B}_5\text{N}_5\text{H}_8$ are produced. These products are boron-nitrogen analogues of diphenyl and naphthalene respectively.



4. Formation of adduct: Borazine forms an adduct with CH_3OH . This adduct undergoes pyrolysis with the elimination of H_2 and gives B-trimethoxy-borazine.



5. Reaction with aniline: Borazine undergoes a strongly exothermic reaction with Aniline to produce tri-aminoborane.



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Poly(borazine): Another example of inorganic polymer is the poly(borazine) chain, with repeat unit $-BRNR-$. The synthesis of tractable, unbranched polymers of this type is complicated by the formation of borazines, which are very stable cyclic molecules, $[(RBRN)_3]$. This problem can possibly be overcome through the use of cyclic mono- and diborolamines. Some of these polymers are thermally stable, up to approximately $500\text{ }^\circ\text{C}$, but are easily hydrolyzed. Their most important use is probably as precursors to boron nitride ceramics. A related polymer is polyborazylene, which is a cyclo-linear boron-nitrogen analogue of polyphenylene. The simplest structure proposed, which corresponds to $[-B_3N_3H_4-]_x$, is shown below. Two final examples are boron nitride itself, $-BN-$, and boron phosphide. Boron nitride can be prepared by heating borax ($Na_2B_4O_7$) in the presence of ammonium chloride at $1000\text{ }^\circ\text{C}$. It is thought to have a planar structure similar to that of graphite. It can be converted into a cubic, diamond-like structure called borazon. It is resistant to hydrolysis and oxygen, and can be harder than diamond. Also, it can be used at temperatures as high as $2000\text{ }^\circ\text{C}$. It is used mainly as a refractory material, abrasive, or insulator.

